DECLARATION

I, Chizuko IKEDA, declare that I reside at 5-50-301, Makita-cho, Takatsuki-shi, Osaka 569-0855 Japan;

That I am familiar with the English and Japanese languages;

That I have prepared a translation of Japanese Patent Application No. 2003-345297, "複合成形体及びその製造方法, MOLDED COMPOSITE ARTICLE AND PROCESS FOR PRODUCING THE SAME"; said translation thereof being attached hereto and made a part of this declaration;

That to the best of my knowledge and belief, the attached translation is accurate and fairly reflects the contents and meaning of the foregoing Japanese language document.

I declare, under penalty of perjury under the laws of the United States of America, that the foregoing is true and correct.

Executed, on November 15, 2011.

Chizuko Ikeda

Chizuko IKEDA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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[Attached Documents]

[Item]	Claims	one copy
[Item]	Description	one copy
[Item]	Abstract	one copy

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[Document Name] Claims

[Claim 1]

A molded composite article in which a resin member comprising a polyamide-series resin and a resin member comprising a thermoplastic polyurethane-series resin are directly joined with each other, wherein the polyamide-series resin comprises a polyamide component having an alicyclic ring.

[Claim 2]

A molded composite article according to Claim 1, wherein the polyamide component having an alicyclic ring is at least one member selected from the group consisting of an alicyclic polyamide-series resin and an alicyclic polyamide elastomer.

[Claim 3]

A molded composite article according to Claim 1, wherein the polyamide component having an alicyclic ring comprises

an alicyclic polyamide component which is at least one member selected from the group consisting of an alicyclic polyamide-series resin, an alicyclic polyamide elastomer and an alicyclic polyamide oligomer; and

a non-alicyclic polyamide component which is at least one member selected from the group consisting of an aliphatic polyamide-series resin and an aromatic polyamide-series resin.

[Claim 4]

A molded composite article according to Claim 1, wherein the polyamide component having an alicyclic ring is obtainable by using an alicyclic diamine as a diamine component.

[Claim 5]

A molded composite article according to Claim 1, wherein the proportion (molar ratio) of an alicyclic monomer residue relative to other monomer residue in all polyamide components constituting the polyamide-series resin is the former/the latter = 100/0 to 0.1/99.9.

[Claim 6]

A molded composite article according to Claim 1, wherein the polyamide-series resin has an amino group in a concentration of not less than 10 mmol/kg.

[Claim 7]

A molded composite article according to Claim 1, wherein the thermoplastic polyurethane-series resin comprises at least one member selected from the group consisting of a polyester urethane elastomer and a polyether urethane elastomer.

[Claim 8]

A molded composite article according to Claim 1, which is a shoe member or a machine part member.

[Claim 9]

A process for producing a molded composite article recited in Claim 1, which comprises

heating at least one resin selected from the group

consisting of the polyamide-series resin and the thermoplastic polyurethane-series resin recited in Claim 1, and

joining the polyamide-series resin and the thermoplastic polyurethane-series resin with each other.

[Claim 10]

A process according to Claim 9, which comprises

heating at least one resin selected from the group consisting of the polyamide-series resin and the thermoplastic polyurethane-series resin to be molten,

bringing at least one resin in the molten state into contact with the other resin, and

joining both resins with each other.

[Claim 11]

A process according to Claim 9, wherein the polyamide-series resin and the thermoplastic polyurethane-series resin are joined with each other in the molding process by a molding method selected from the group consisting of a thermoforming, an injection molding, an extrusion molding, and a blow molding.

[Document Name] Description

[Title of the Invention] MOLDED COMPOSITE ARTICLE AND PROCESS FOR PRODUCING THE SAME

[Technical Field]

[0001]

The present invention relates to a molded composite article (or composite molded article) in which a resin member which comprises a polyamide-series resin comprising a polyamide component having an alicyclic ring is joined to a resin member comprising a thermoplastic polyurethane-series resin in a one-piece construction without an adhesive, and a process for producing the same.

[Background Art]

[0002]

In order to improve design or decorative property or excellent touch or texture (e.g., soft texture), or in order to impart higher functionalities, there have been proposed composites (molded composite articles) formed with a combination of a plurality of resins each having a different hardness, for example, a molded composite article in which at least a part of a resin molded article is coated with a thermoplastic elastomer. Such a molded composite article is usually produced by adhesion of a plurality of molded members through an adhesive. For example, Japanese Patent Application Laid-Open No. 267585/1996 (JP-8-267585A) (Patent document 1) discloses a resin molded article in which a plurality of resin molded articles formed with a

polyamide resin or others are weld or adhered to each other through a finishing agent such as a urethane polymer or a urethane-series adhesive. However, such a process using an adhesive is not only uneconomical due to complicated steps, but also has problems such as environmental pollution by an organic solvent or others. Furthermore, in the case where such a resin molded article is small in adhesive area or needs (or requires) fine patterns, production of such a resin molded article on a commercial or industrial basis is difficult because not only a coating step of an adhesive becomes quite complicated, but also bonded strength or bonded stability of the resin molded article is insufficient.

[0003]

On the other hand, from the viewpoint of rationalization of production processes or environmental protection, a process for direct thermal fusing of a plurality of molded members has been adopted. The molded composite article obtained by thermal fusing is usually manufactured by a molding process such as a two-color (or double) molding or an insert molding. However, in such a molding process, combination of materials which are acceptable for thermal fusing is significantly limited, and in many cases the combination is only limited to the same kind of materials. Moreover, it is not easy to establish molding conditions for obtaining enough bonded strength. Therefore, in order to reinforce the fused part,

such a method is utilized in addition to thermal fusing or welding, that a method for preparing a concavo-convex site (or part) in an area to be bonded of the molded member for mechanical joining, a method for chemically activating a surface of the molded member by a corona discharge treatment or the like. In such a method, however, the molded composite article is deteriorated in flexuous property. Moreover, the method tends to require a complicated structure of the molded member, or increases the number of production steps. As a result, such a method has many disadvantages in quality of product and economic circumstances.

[0004]

In order to solve these problems, it has been investigated to use, as a material for a resin member constituting a molded composite article, a thermoplastic polyurethane resin having a relatively excellent adhesiveness itself with a focus on usage (or purpose) of shoe(s) and others. For example, Japanese Patent Application Laid-Open No. 248201/1997 (JP-9-248201A) (Patent document 2) proposes a centroid body for a cycling shoe, which comprises a shoe sole member formed with a polyamide resin reinforced with a glass fiber as an insert, wherein a sidewall of the shoe sole member is molded with a polyurethane resin. However, since such a usage exposes the centroid body to a mechanically severe condition, the reference describes in Examples, that a through-hole in the polyamide resin shoe sole member is needed for mechanical

conjunction of the sole member with the polyurethane resinous sidewall member.

[0005]

Moreover, Japanese Patent Application Laid-Open No. 308205/1995 (JP-7-308205A) (Patent document 3) proposes a shoe sole reinforced by replacing at least a part of the outsole composed of a polyurethane resin with a fiber reinforced polyamide resin sheet. This reference discloses that the polyamide resin comprises a mixture of a polyamide and a polyolefin (an ionomer) in order to obtain bonding or joining properties tolerant to heavy bending of the shoe sole. As apparent from these references, for the usage of shoe soles and others which require excellent mechanical properties or bending or flexing fatigue resistance, it has been watched to combine a thermoplastic polyurethane resin excellent in bonding properties by itself and a polyamide resin surpassing in mechanical properties. In general, since a thermoplastic polyurethane-series resin itself has a bondability to a polyamide-series resin to a certain degree, in adequate conditions such as material temperature in bonding or others, a molded composite article is obtainable which has a bonded strength durable to the practical use. However, in the case where high bending or flexing fatigue resistance is required to the bonded surface, or where using environment of bonded member is extremely severe, much higher (one-step higher) bonded strength than the above molded composite article is required. That is,

bondability (strength) of members obtained by thermal fusing or welding is insufficient, and further ingenuity or improvement is necessary.

[0006]

Among the field of these shoe soles, in the field of athletic shoe such as a succor, baseball, or basketball shoe, in order to obtain higher flexibility as a shoe sole as well as strong bondability between materials, there is widely employed a molded composite article combining a polyurethane resin and a polyamide-series elastomer having not only high flexibility and toughness but also excellent bondability (that is, an elastomer in which a polyamide-series resin is softened by introduction of a polyether component).

[0007]

For example, Japanese Patent Application Laid-Open No. 505333/1996 (JP-8-505333A) (Patent document 4) discloses that a lightened shoe sole is obtained by injection-molding a polyamide elastomer containing a foaming agent into a mold, with inserting or putting a molded article of a thermoplastic resin such as a polyether amide, a polyether ester or a polyurethane in a mold, and adhering to the thermoplastic resin molded article (un-lightweight (un-lightened) plastic) and the elastomer (lightweight thermoplastic elastomer). However, even in such a combination using the polyamide-series elastomer, the adhesive strength has not been enough yet. Therefore, such

a composite is affected by not only conditions for molding or conditions of materials to be used (e.g., production lot) but also using environment of the product (molded composite article), resulting in unstableness of the bonded strength or the duration of the molded composite article (particularly the duration of the adhered site).

[0008]

Moreover, among the combinations of the polyurethane resin and the polyamide-series elastomer, in both practical use in market and the examples of the Patent Document 4, a polyether-series polyurethane resin is used as the polyurethane resin, and as a matter of fact, the composite comprising a polyester-series polyurethane resin and a polyamide-series elastomer is not produced. The reason is that both the polyurethane resin and the polyamide-series elastomer have the same series of a polyether segment in molecules thereof and the polyether segment content of the polyether-series polyurethane is larger than that of the polyester-series polyurethane. That is, the polyether-series polyurethane ensures high bonding or joining properties to a polyamide-series elastomer due to a sufficient cohesion derived from a higher similarity of a molecule thereof; on the other hand, the polyester-series polyurethane probably lacks such a cohesion. However, the polyester-series polyurethane resin is excellent in mechanical properties and economical efficiency than the polyether-series polyurethane resin. Therefore, not

limited to the market of an athletic shoe, in all the field utilizing a composite of a polyurethane-series resin and a polyamide-series resin, it is a great issue in terms of both technical and commercial subjects that both polyether-series polyurethane resin and a polyester-series polyurethane resins are used with no distinction in technology development for a composite.

[0009]

Further, Japanese Patent Application Laid-Open No. 273826/2002 (JP-2002-273826A) (Patent document 5) discloses a composite comprising a combination of a vulcanized rubber member in which a rubber is vulcanized with a radical-generating agent and a resin member comprising a thermoplastic resin having at least two hydrogen or sulfur atoms per molecule on average, wherein the hydrogen or sulfur atom has an orbital interaction energy coefficient S of not less than 0.006. However, this method needs compulsory contact both members with each other with heating both members (usually at a temperature of not less than 160°C) for a given length of time (usually not less than 7 minutes) due to necessity of a crosslinking agent for binding both members. Therefore, in fact, in some final product configurations of the composite, this method is unusable for a material having low heat-resistance, particularly the material having a deflection temperature of not more than 100°C under a load of 0.45MPa defined by ISO 175. Moreover, in the case of using a material having

relatively a high heat-resistance, it is difficult to obtain a molded composite article having a high dimensional accuracy because the exposure to the condition of a high temperature and a high pressure for a long period inevitably causes physical developments such as expansion and contraction in the molded composite article.

[Patent Document 1] JP-8-267585A

[Patent Document 2] JP-9-248201A

[Patent Document 3] JP-7-308205A

[Patent Document 4] JP-8-50533A

[Patent Document 5] JP-2002-273826A

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0010]

It is therefore an object of the present invention to provide a composite article comprising a polyamide-series resin member and a thermoplastic polyurethane-series resin member, in which the bonded strength between the both members are dramatically improved; and a process for producing the same.

[0011]

It is another object of the present invention to provide a composite article comprising a polyamide-series resin member and a thermoplastic polyurethane-series resin member, in which the both members are firmly joined or bonded together regardless of kinds of the thermoplastic polyurethane-series resin to be used; and a process for

producing the same.

[0012]

It is still another object of the present invention to provide a molded composite article in which a polyamide-series resin member and a thermoplastic polyurethane-series resin member are firmly joined together by thermal fusing in a convenient manner for a short period without going through complicated production steps; and a process for producing the same.

[Means to Solve the Problems]

[0013]

The inventors of the present invention made intensive studies to achieve the above objects and finally found that introduction of an alicyclic ring (or an aliphatic ring) to at least a part of a polyamide component constituting a polyamide-series resin realizes extremely higher bonded strength to a thermoplastic polyurethane-series resin than a polyamide-series resin comprising a general aliphatic amide component, and further ensures, regardless of the kinds of polyurethane-series resins, firm or strong joining of the polyamide-series resin to a polyester-series polyurethane resin in the similar (or comparable) joining degree with a polyether-series polyurethane resin. The present invention was accomplished based on the above findings.

[0014]

That is, the molded composite article of the present

invention is a molded composite article in which a resin member comprising a polyamide-series resin and a resin member comprising a thermoplastic polyurethane-series resin are directly joined with each other, wherein the polyamide-series resin comprises a polyamide component having an alicyclic ring. The polyamide component may comprise an alicyclic polyamide-series resin, an alicyclic polyamide elastomer, and the like. Moreover, the polyamide component may comprise an alicyclic polyamide component (such as an alicyclic polyamide-series resin, an alicyclic polyamide elastomer or an alicyclic polyamide oligomer) and a non-alicyclic polyamide component (such as an aliphatic polyamide-series resin or an aromatic polyamide-series resin). The polyamide-series resin having the alicyclic ring may be a polyamide component obtained by using an alicyclic diamine as a diamine component. The proportion (molar ratio) of an alicyclic monomer residue relative to other monomer residue in all polyamide components constituting the polyamide-series resin may be the former/the latter = about 100/0 to 0.1/99.9. The polyamide-series resin may have an amino group in a concentration of not less than 10 mmol/kg. The thermoplastic polyurethane-series resin may be a polyester urethane elastomer or a polyether urethane elastomer.

[0015]

The molded composite article of the present invention is suitable for a component member of a shoe or a machine

part (e.g., a roll).

[0016]

Such a molded composite article may be produced by heating at least one resin selected from the group consisting of the polyamide-series resin and thermoplastic polyurethane-series resin, and joining the polyamide-series resin and the thermoplastic polyurethane-series resin with each other. For example, by heating at least one resin selected from the group consisting of the polyamide-series resin and the thermoplastic polyurethane-series resin to be molten, and bringing at least one resin in the molten state into contact with the other resin, both resins may be joined (or bonded) with each other. Moreover, the polyamide-series resin and the thermoplastic polyurethane-series resin may be joined with each other in the molding process by a molding method selected from the group consisting of a thermoforming, an injection molding, an extrusion molding, and a blow molding.

[0017]

Incidentally, throughout this specification, the meaning of the term "resin" includes "a resin composition". Moreover, throughout this specification, the term "adhesion (or adhering)" means a technique for compounding a plurality of members through an adhesive, the term "joining (or bonding)" means a technique for compounding a plurality of members without an adhesive, and the both terms are distinguished from each other. Fusing (or thermal fusing)

is one embodiment of joining.

[Effects of the Invention]

[0018]

In the present invention, the composite article comprising a polyurethane-series resin member and a polyamide-series resin member ensures to have the significantly improved bonded strength (or joined strength) between both resin members. Moreover, independent of the species of thermoplastic polyurethane-series resin to be used, both resin members can be firmly joined or bonded with each other. Accordingly, for example, a composite article comprising a polyurethane-series resin member having excellent mechanical properties and a polyamide-series elastomer member or the like, is also useful for the field of an athletic shoe requiring flexibility or plasticity of whole composite article. Further, according to the process of the present invention, a molded composite article is producible in which a polyamide-series resin member and a thermoplastic polyurethane resin member are firmly joined together by thermal fusing in a short period of time in a simple manner without going through complicated production steps.

[Preferred Embodiment of the Invention]

[0019]

[Molded composite article]

The molded composite article of the present invention comprises a resin member comprising a polyamide component

having an alicyclic ring and a resin member comprising a thermoplastic polyurethane-series (or -based) resin and directly joined with the polyamide-series resin member.

[0020]

(Polyamide-series resin)

The polyamide-series resin in the present invention comprises a polyamide component having an alicyclic ring. As such a polyamide component, there may be exemplified (1) a single use of an alicyclic polyamide component such as an alicyclic polyamide-series resin or an alicyclic polyamide elastomer, or an alloy or blend (mixture) thereof, and (2) a polyamide-series resin composition comprising an alicyclic polyamide component (such as an alicyclic polyamide-series resin, an alicyclic polyamide elastomer, or an alicyclic polyamide oligomer) and a non-alicyclic polyamide component such as an aliphatic polyamide-series resin or an aromatic polyamide-series resin.

[0021]

(1) Single use of alicyclic polyamide component or a combination thereof

The alicyclic polyamide component may be a single component of an alicyclic polyamide-series resin or elastomer, or may be an alloy or blend component in which an alicyclic polyamide-series resin and an alicyclic polyamide elastomer are combined.

[0022]

The alicyclic polyamide-series resin is an alicyclic

polyamide-series resin having an alicyclic ring in the main chain or side chain of the molecule, and usually has an alicyclic ring in the main chain. As the alicyclic polyamide-series resin, for example, an alicyclic polyamide can be employed which is obtainable by using at least one alicyclic monomer selected from the group consisting of an alicyclic diamine and an alicyclic dicarboxylic acid as a monomer component. The alicyclic polyamide may be either a homopolyamide or a copolyamide.

[0023]

The alicyclic polyamide-series resin may be a polyamide obtainable from polymerization of the alicyclic monomers, or may be obtained by polymerization of the alicyclic monomer and other copolymerizable monomer. The other copolymerizable monomer may be an aromatic monomer such as an aromatic diamine or an aromatic dicarboxylic acid, and preferably an aliphatic monomer such as an aliphatic diamine and/or an aliphatic dicarboxylic acid from the viewpoint of flexibility or plasticity. Further, in terms of joinability, an alicyclic diamine is preferably used as the alicyclic monomer, and the combination of an alicyclic diamine and an aliphatic dicarboxylic acid is particularly preferred. The alicyclic polyamide-series resin obtained from the alicyclic monomer and an aliphatic monomer together is high in transparency, and is known as a so-called transparent polyamide.

[0024]

As the alicyclic diamine, there may be exemplified a saturated alicyclic diamine [e.g., a diaminocycloalkane (preferably a diaminoC_{5-12}cycloalkane) such as diaminocyclopentane, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, 1,2-diaminocyclohexane, diaminocycloheptane, or hydrogenated naphthalenediamine], an unsaturated alicyclic diamine [e.g., a diaminocycloalkene (preferably C_{5-12}cycloalkene) such as 1,2-diaminocyclohexene, or 1,3-diaminocyclohexene], a hydrogenated diphenyl-series diamine [e.g., a bis(aminocycloalkyl)alkane (preferably a bis(aminoC_{5-8}cycloalkyl)C_{1-6}alkane) such as 4,4'-diaminohydrogenated biphenyl, bis(4-aminocyclohexyl)methane, bis(4-amino-3-methylcyclohexyl)methane, bis(4-amino-2-methylcyclohexyl)methane, or 2,2-bis(4-aminocyclohexyl)propane; a bis(4-aminocycloalkane)cycloalkane (preferably a bis(aminoC_{5-8}cycloalkyl)C_{5-12}cycloalkane) such as bis(4-aminocyclohexyl)cyclohexane; bis(4-aminocyclohexyl)ketone; bis(4-aminocyclohexyl)sulfoxide; and 4,4'-diaminodicyclohexylether], a crosslinked cyclic alkanediamine (e.g., a di- or tricycloC_{7-10}alkane-diamine such as bornanediamine, norbornanediamine, or adamantanediamine), a crosslinked cyclic alkene-diamine (e.g., a di- or tri cycloC_{7-10}alkene-diamine such as

bornenediamine or norbornenediamine), and others. These alicyclic diamines can be used singly or in combination. Among these alicyclic diamines, a diamine containing an aminoC_{5-10}cycloalkane, particularly a C_{6-8}cycloalkanediamine or a bis(C_{6-8}cycloalkyl)C_{1-4}alkanediamine is preferred.

[0025]

The diamine component may also include an aliphatic diamine or an aromatic diamine. The aliphatic diamine may include, for example, a C_{4-16}alkylenediamine (preferably a C_{4-14}alkylenediamine, particularly a C_{6-12}alkylenediamine) such as tetramethylenediamine, hexamethylenediamine, or dodecanediamine. The aromatic diamine may include, for example, methaxylylenediamine, phenylenediamine and others. These diamine components can be used singly or in combination. Among these diamine components, the aliphatic diamine is preferred from the viewpoint of flexibility or plasticity.

[0026]

As the alicyclic dicarboxylic acid, there may be exemplified a saturated alicyclic dicarboxylic acid [e.g., a cycloalkanedicarboxylic acid (preferably a C_{5-12}cycloalkane-dicarboxylic acid) such as cyclopenetanedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, cyclohexane-1,3-dicarboxylic acid, cyclohexane-1,2-dicarboxylic acid, or

cycloheptanedicarboxylic acid], an unsaturated alicyclic dicarboxylic acid [e.g., a cycloalkenedicarboxylic acid (preferably a C_{5-12}cycloalkene-dicarboxylic acid) such as cyclohexene-1,2-dicarboxylic acid or cyclohexene-1,3-dicarboxylic acid], a hydrogenated diphenyl-series dicarboxylic acid [e.g., a bis(carboxycycloalkyl)alkane (preferably a bis(carboxyC_{5-8}cycloalkyl)C_{1-6}alkane) such as hydrogenated biphenyl-4,4'-dicarboxylic acid, bis(4-carboxycyclohexyl)methane, bis(4-carboxy-3-methylcyclohexyl)methane, bis(4-carboxy-2-methylcyclohexyl)methane, or 2,2-bis(4-carboxycyclohexyl)propane; bis(4-carboxycyclohexyl)ketone; bis(4-carboxycyclohexyl)sulfoxide; and 4,4'-dicarboxydicyclohexyl ether], a crosslinked cyclic alkanedicarboxylic acid (a di- or tricycloC_{7-10}alkane-dicarboxylic acid such as bornanedicarboxylic acid, norbornanedicarboxylic acid, or adamantanedicarboxylic acid), a crosslinked cyclic alkenedicarboxylic acid (a di- or tricycloC_{7-10}alkene-dicarboxylic acid such as bornenedicarboxylic acid or norbornenedicarboxylic acid), and others. Among these alicyclic dicarboxylic acids, a dicarboxylic acid containing a C_{5-10}cycloalkane, particularly a C_{6-8}cycloalkane-dicarboxylic acid or a bis(C_{6-8}cycloalkyl)C_{1-4}alkane-dicarboxylic acid is

preferred.

[0027]

The dicarboxylic acid component may also include an aliphatic dicarboxylic acid or an aromatic dicarboxylic acid. As the aliphatic dicarboxylic acid, for example, there can be mentioned an alkanedicarboxylic acid having 4 to 20 carbon atoms (preferably a C_{4-16}alkanedicarboxylic acid, particularly a C_{6-14}alkanedicarboxylic acid) such as succinic acid, glutaric acid, adipic acid, pimeric acid, cork acid (suberic acid), azelaic acid, sebacic acid, or dodecanedioic acid. The aromatic dicarboxylic acid may include, for example, an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, phthalic acid, and others. These dicarboxylic acid components can be used singly or in combination. Among these dicarboxylic acid components, the aliphatic dicarboxylic acid is preferred from the viewpoint of flexibility.

[0028]

In the alicyclic polyamide-series resin, the proportion (or molar ratio) of an alicyclic monomer residue relative to other copolymerizable monomer residue is, [the alicyclic monomer residue/the copolymerizable monomer residue] = about 100/0 to 0.1/99.9, preferably about 90/10 to 0.5/99.5 (e.g., 70/30 to 1/99), and more preferably about 60/40 to 3/97 (particularly about 50/50 to 5/95). In terms of joinability, the proportion of the alicyclic monomer residue is preferred to be large, but in terms of flexibility,

the proportion of the alicyclic monomer residue is preferred to be small. Therefore, it is preferred to select appropriate proportions of the alicyclic monomer residue depending on the purpose.

[0029]

Moreover, the alicyclic monomer may be added only to terminal (end) group of the polymer. The method for addition may include for example a method which comprises blocking or capping a terminal group of an after-mentioned aliphatic or aromatic polyamide with a carboxyl group and adding an aliphatic diamine to the terminal carboxyl group(s), or a method which comprises polymerizing a lactam having about 4 to 20 carbon atoms (such as caprolactam or lauryllactam (dodecyllactam)) in the presence of a small amount of a dicarboxylic acid component, followed by adding an alicyclic diamine to the terminal carboxyl group(s), and others.

[0030]

Among these alicyclic polyamide-series resins, as mentioned above, from the viewpoint of joinability and flexibility, it is preferred to use an alicyclic polyamide-series resin obtainable from an alicyclic diamine and an aliphatic dicarboxylic acid, for example, an alicyclic polyamide-series resin is particularly preferred which is obtained from a diamine containing an aminoC_{5-10}cycloalkane [e.g., a C_{6-8}cycloalkanediamine such as diaminocyclohexane, a

bis(aminoC_{6-8}cycloalkyl)C_{1-4}alkane such as bis(4-aminocyclohexyl)methane, or bis(4-amino-2-methylcyclohexyl)methane], and an alkanedicarboxylic acid having about 4 to 20 carbon atoms (e.g., a C_{6-14}alkanedicarboxylic acid such as azelaic acid, sebacic acid, or dodecanedioic acid).

[0031]

The alicyclic polyamide-series resins can be used singly or in combination. Among the alicyclic polyamide-series resins, a condensation product of the aliphatic dicarboxylic acid with the alicyclic diamine (a homo- or copolyamide) or others is preferred.

[0032]

The number average molecular weight of the alicyclic polyamide-series resin is about 6,000 to 100,000, preferably about 8,000 to 50,000, and more preferably about 10,000 to 30,000. The molecular weight can be adjusted by using excessive amount of aliphatic diamine and/or alicyclic diamine than the calculated amount in the polymerization.

[0033]

The alicyclic polyamide elastomer (alicyclic polyamide block copolymer) may include an alicyclic polyamide elastomer such as an alicyclic polyamide-polyether block copolymer [e.g., an alicyclic polyamide-polyether block copolymer which contains a polyether segment or block as a soft segment, such as a polyC_{2-4}alkylene oxide (e.g., a polytetramethylene oxide

(PTMG), a polyethylene oxide, or a polypropylene oxide)], and others. As the alicyclic polyamide block, a polyamide block (unit) constituting the alicyclic polyamide-series resin can be utilized. The alicyclic polyamide elastomer may be a copolyamide elastomer in which at least one member selected from the group consisting of an alicyclic polyamide block and a polyether block is combined with a block different in species. Moreover, the alicyclic polyamide block and the polyether block may be a copolyamide block and a copolyether block, respectively.

[0034]

As the alicyclic polyamide-polyether block copolymer, there may be mentioned a block copolymer obtainable by copolycondensation of an alicyclic polyamide block having a reactive terminal group with a polyether block having a reactive terminal group, particularly, an alicyclic polyether amide (e.g., a block copolymer of an alicyclic polyamide block having dicarboxyl terminal groups with a polyoxyalkylene block having diamine terminal groups), a polyether ester amide (e.g., a block copolymer of an alicyclic polyamide block having dicarboxyl terminal groups with a polyoxyalkylene block having dihydroxy terminal groups, a block copolymer of an alicyclic polyamide block having diamine terminal groups with a polyoxyalkylene block having dicarboxyl terminal groups (e.g., a polyoxyalkylene block whose terminal groups are esterified with a dicarboxylic acid), and the like.

[0035]

The proportion of the alicyclic monomer constituting the alicyclic polyamide elastomer can be selected from the same range with the alicyclic polyamide-series resin. These alicyclic polyamide elastomers can be used singly or in combination.

[0036]

From the viewpoint of joinability, the alicyclic polyamide elastomer is preferably used in combination with the above-mentioned alicyclic polyamide-series resin. In the case of using the alicyclic polyamide-series resin in combination with the alicyclic polyamide elastomer, the proportion (weight ratio) of the above may be [the alicyclic polyamide-series resin/the alicyclic polyamide-series elastomer] = about 99/1 to 30/70, preferably about 97/3 to 50/50, and more preferably about 95/5 to 60/40.

[0037]

(2) Composition comprising alicyclic polyamide component and non-alicyclic polyamide component

The polyamide component having an alicyclic ring may be a composition comprising an alicyclic polyamide component and a non-alicyclic polyamide component.

[0038]

The alicyclic polyamide component may be the alicyclic polyamide-series resin and the alicyclic polyamide elastomer, in addition an alicyclic polyamide oligomer. These alicyclic polyamide components can be used singly

or in combination.

[0039]

As the alicyclic polyamide oligomer, there may be used an alicyclic polyamide having a relatively low molecular weight, which may be obtained by a conventional manner, for example, by adjusting polycondensation or other conditions and using the above-mentioned alicyclic polyamide component(s). For example, as a polyamide component to be a raw material, there may be mentioned the combination of the above-mentioned diamine with the dicarboxylic acid, the combination of the above-mentioned diamine and/or dicarboxylic acid, with the lactam (e.g., a lactam having about 4 to 20 carbon atoms, such as ω-laurolactam), and other combinations. The alicyclic polyamide oligomer may be obtained by for example polymerizing the lactam and the alicyclic diamine with heating and stirring under an applied pressure.

[0040]

The number average molecular weight of the alicyclic polyamide oligomer may be, for example, about 500 to 10,000, preferably about 1000 to 10,000 (e.g., about 2,000 to 9,000), and more preferably about 3,000 to 8,000 (e.g., about 3,000 to 6,000), and the joining property of the polyamide-series resin constituting the resin member to the thermoplastic polyurethane can be improved by using an alicyclic polyamide oligomer having such a relatively high molecular weight. The above-mentioned number average molecular weight may

be adjusted by using an excessive amount of aliphatic diamine and/or alicyclic diamine than the calculated amount in the polymerization.

[0041]

Among these alicyclic polyamide components, in terms of joinability, the alicyclic polyamide-series resin or the alicyclic polyamide oligomer, particularly the alicyclic polyamide-series resin is preferred. Moreover, from the viewpoint of joinability, the polyamide component obtained by using an alicyclic diamine (e.g., a diamine containing an aminoC_{5-10}cycloalkane) is preferred as the alicyclic polyamide component.

[0042]

As the non-alicyclic polyamide component, there may be mentioned an aliphatic polyamide-series resin or an aromatic polyamide-series resin, and various homopolyamides and copolyamides can be employed.

[0043]

Among the aliphatic polyamide-series resins, the homopolyamide may include a condensation product of the aliphatic diamine component and the aliphatic dicarboxylic acid component, for example, a polyamide 46, a polyamide 66, a polyamide 610, a polyamide 612, and a polyamide 1010; a homopolyamide of a lactam [e.g., a lactam having about 4 to 20 (preferably about 4 to 16) carbon atoms, such as ε-caprolactam or ω-laurolactam] or an aminocarboxylic acid [e.g., an aminocarboxylic acid having about 4 to 20

(preferably about 4 to 16) carbon atoms, such as ω-aminoundecanoic acid], for example, a polyamide 6, a polyamide 11, and a polyamide 12; and others. Moreover, the copolyamide may include a copolyamide which can be obtained by copolymerization of a monomer component capable of constituting a polyamide, e.g., the aliphatic diamine components, the aliphatic dicarboxylic acid components, the lactams and the aminocarboxylic acids. Examples of the copolyamide may include a copolymer of 6-aminocaproic acid and 12-aminododecanoic acid; a copolymer of 6-aminocaproic acid, 12-aminododecanoic acid, hexamethylenediamine and adipic acid; a copolymer of hexamethylenediamine, adipic acid, hydrogenated dimer acid and 12-aminododecanoic acid; a polyamide 6/11, a polyamide 6/12, a polyamide 66/11, a polyamide 66/12; and others. These aliphatic polyamide-series resins can be used singly or in combination.

[0044]

The aromatic polyamide-series resin may include a polyamide in which at least one component selected from the aliphatic diamine component and the aliphatic dicarboxylic acid component comprises an aromatic component, for example, a polyamide having an aromatic component in a diamine component [for example, a condensation product of an aromatic diamine (e.g., metaxylylenediamine) and an aliphatic dicarboxylic acid, such as MXD-6], a polyamide having an aromatic component in a dicarboxylic acid

component [e.g., a condensation product of an aliphatic diamine (e.g., trimethylhexamethylenediamine) and an aromatic dicarboxylic acid (e.g., terephthalic acid, isophthalic acid)], and others. These aromatic polyamide-series resins can be used singly or in combination.

[0045]

Incidentally, in the non-alicyclic polyamide component, a polyamide in which both a diamine component and a dicarboxylic acid component comprise an aromatic component [for example, a perfect aromatic amide such as a poly(m-phenyleneisophthalamide) (e.g., Aramid)] may be used in combination.

[0046]

The non-alicyclic polyamide component may further include a polyamide comprising a dimer acid as a dicarboxylic acid component, a polyamide in which a branched chain structure is introduced by using a small amount of a polyfunctional polyamine and/or polycarboxylic acid component, a modified polyamide (e.g., a N-alkoxymethylpolyamide), an aliphatic or aromatic polyamide block copolymer, and others.

[0047]

These non-alicyclic polyamide components can be used singly or in combination. Among these components, in terms of flexibility, the aliphatic polyamide-series resin or the aliphatic polyamide block copolymer, particularly the

aliphatic polyamide-series resin can be preferably employed.

[0048]

The proportion (weight ratio) of the alicyclic polyamide component relative to the non-alicyclic polyamide component may be, depending on the proportion of the alicyclic ring in the alicyclic polyamide component, selected from the range of the former/the latter = about 99/1 to 1/99, and in terms of joinability, the proportion may be, for example, about the former/the latter = about 98/2 to 30/70, preferably about 97/3 to 50/50, and more preferably about 95/5 to 70/30. Moreover, in the case where the alicyclic polyamide component comprises an alicyclic polyamide oligomer, even a small proportion thereof ensures sufficient joinability. Accordingly, from the viewpoint of flexibility or others, the proportion of the alicyclic polyamide component relative to the non-alicyclic polyamide component may be, for example, the former/the latter = about 50/50 to 0.1/99.9, preferably about 40/60 to 3/97, and more preferably about 30/70 to 5/95 (particularly about 20/80 to 5/95).

[0049]

In these polyamide components having an alicyclic ring, in terms of joinability, is preferred a component containing an alicyclic polyamide-series resin, particularly (i) an alicyclic polyamide-series resin, (ii) a combination of an alicyclic polyamide-series resin with

an alicyclic polyamide elastomer, or (iii) a combination of an alicyclic polyamide-series resin with an aliphatic polyamide-series resin.

[0050]

In the present invention, the polyamide component having an alicyclic ring may have an amino group at a specific concentration. The amino group usually shows a free amino group (-NH_2 group) and usually does not include a -NH- (imino) group and -N< group derived from an amide bond constituting the main chain of the polyamide-series resin, a urea bond, a urethane bond and other bond. The polyamide-series resin may have the free amino group in a branched chain thereof, or at the end of a main chain thereof.

[0051]

The content (or concentration) of the amino group (or amino group concentration) in the polyamide-series resin having an alicyclic ring is, relative to 1 kg of the polyamide-series resin, not less than 10 mmol (e.g., about 10 to 300 mmol), preferably not less than 15 mmol (e.g., about 15 to 200 mmol), more preferably not less than 20 mmol (e.g., about 20 to 150 mmol), and particularly not less than 30 mmol (e.g., about 30 to 100 mmol).

[0052]

The polyamide-series resin may preferably contain an amino group in the above range, particularly contain a terminal amino group in the above range. The amino group may be an alicyclic amino group in which a part of or all

terminal amino groups is (are) an alicyclic amino group. Moreover, in order to adjust the content (concentration) of amino groups, in addition to an amine compound [e.g., a diamine (e.g., the above exemplified aliphatic diamines, the alicyclic diamines and the aromatic diamines), a polyamine such as an aliphatic polyamine (for example, a polyalkylenepolyamine (e.g., a polyC_{2-3}alkylenepolyamine) such as diethylenetriamine or triethylenetetramine)] or others may be added.

[0053]

In the present invention, it is particularly preferred to use the alicyclic diamine for converting the amino group into an alicyclic amino group (e.g., a cycloalkylamino group) derived from the alicyclic diamine. Usage of the polyamide component having the alicyclic amino group derived from an alicyclic diamine improves joinability (or bonding strength) of the polyamide-series resin to the thermoplastic polyurethane-series resin member.

[0054]

Incidentally, the concentration of the carboxyl group in the polyamide component having an alicyclic ring is not particularly limited to a specific one, and for example about 0.1 to 200 mmol/kg, preferably about 0.5 to 150 mmol/kg, and more preferably about 1 to 100 mmol/kg.

[0055]

In the present invention, the proportion (molar ratio) of the alicyclic monomer residue relative to the other

monomer residue in all polyamide components constituting the polyamide-series resin is the former/the latter = about 100/0 to 0.1/99.9, preferably about 90/10 to 0.5/99.5, and more preferably about 70/30 to 1/99.

[0056]

In such a range that the effects of the present invention are not deteriorated, the polyamide-series resin member may contain other resins [e.g., a thermoplastic resin such as a polyester-series resin, a polycarbonate-series resin, a polysulfone-series resin, a polyimide-series resin, a polyketone-series resin, a polyolefinic resin, a styrenic resin, a (meth)acrylic resin, or a halogen-containing vinyl-series resin], and various additives, for example, a filler or reinforcing agent (e.g., a reinforcing fiber), a stabilizer (e.g., a ultraviolet ray absorbing agent, an antioxidant, and a heat stabilizer), a coloring agent, a plasticizer, a lubricant, a flame retardant, an antistatic agent, and others.

[0057]

Incidentally, in the case of producing the molded composite article of the present invention, a "warp" in the product sometimes occurs in association with joining due to the difference between mold shrinkage factors of the resin members. In the case where the degree of the correction for the warp is large, there is a possibility that breaking of the joining part or generation of stress crack in each resin member occurs. Therefore, the

polyamide-series resin having an alicyclic ring preferably has lower crystallinity. In the polyamide-series resin, the final crystallinity degree (mean final crystallinity degree) is advantageously not more than 50% (e.g., about 5 to 50%), preferably not more than 40% (e.g., about 5 to 40%), and more preferably not more than 30% (e.g., about 10 to 30%).

[0058]

Incidentally, considering only the final crystallinity degree, the copolymer is more advantageous than the homopolymer. Further, in general the copolymer is also more advantageous than the homopolymer from the perspective that the copolymer is superior to the homopolymer in flexibility.

[0059]

In the case of a polyamide block copolymer (a polyamide elastomer) which comprises a polyamide homopolymer as a hard segment and a polyether as a soft segment, the final crystallinity degree can be adjusted by the ratio of the hard segment and the soft segment. When the final crystallinity degree of the polyamide block copolymer is adjusted to not more than 40% (e.g., about 5 to 40%), preferably not more than 35% (e.g., about 5 to 35%) and more preferably not more than 30% (e.g., about 10 to 30%), such a copolymer is advantageously used in combination with a thermoplastic polyurethane-series resin member for inhibiting warp generation, and further can provide a

flexibility which suits with that of a thermoplastic polyurethane-series resin.

[0060]

Incidentally, the term "the final crystallinity degree" means a degree of crystallinity measured by an X-ray diffraction analysis using a flat plate 1 mm thick, where the flat plate is formed by heating a sample resin to a temperature which is 20°C higher than a melting point thereof, and then cooling the resin to a room temperature at a rate of 3°C/minute by means of a precision (or accurate) heat pressing machine. The melting point of the resin is measured by a differential scanning calorimeter (DSC apparatus) in accordance with JIS K 7122.

[0061]

(Polyurethane-series resin)

The thermoplastic polyurethane-series resin may be obtained by reacting a diisocyanate, a diol and, if necessary, a chain-extension agent.

[0062]

The diisocyanate may include an aliphatic diisocyanate such as hexamethylene diisocyanate (HMDI), or 2,2,4-trimethylhexamethylene diisocyanate; an alicyclic diisocyanate such as 1,4-cyclohexane diisocyanate, a dicycloalkylmethane-4,4'-diisocyanate, or isophorone diisocyanate (IPDI); an aromatic diisocyanate such as phenylene diisocyanate, tolylene diisocyanate (TDI), or diphenylmethane-4,4'-diisocyanate (MDI); an

araliphatic diisocyanate such as xylylene diisocyanate; and others. As the diisocyanate, there may also be used a compound having an alkyl group (e.g., methyl group) substituted on a main chain or ring thereof. The diisocyanate(s) may be used singly or in combination.

[0063]

Examples of the diol may include a polyester diol [for example, a polyester diol (aliphatic polyester diol) derived from an aliphatic dicarboxylic acid component (e.g., a C_{4-12}aliphatic dicarboxylic acid such as adipic acid), an aliphatic diol component (e.g., a C_{2-12}aliphatic diol such as ethylene glycol, propylene glycol, butanediol, or neopentyl glycol), and/or a lactone component (e.g., a C_{4-12}lactone such as ε-caprolactone), e.g., a poly(ethylene adipate), a poly(1,4-butylene adipate), and a poly(1,6-hexane adipate), a poly-ε-caprolactone], a polyether diol [for example, an aliphatic polyether diol, e.g., a poly(oxyC_{2-4}alkylene) glycol such as a polyoxyethylene glycol, a poly(oxytrimethylene) glycol, a polyoxypropylene glycol, or a polyoxytetramethylene glycol, and a block copolymer of the poly(oxyalkylene) glycol (e.g., a polyoxyethylene-polyoxypropylene block copolymer); an aromatic polyether diol, e.g., an adduct of an aromatic diol with an alkylene oxide, such as a bisphenol A-alkylene oxide adduct (e.g., an adduct of a C_{2-4}alkylene oxide such as ethylene oxide, or propylene oxide)]; a polyester ether diol (a polyester diol obtained by using

the polyether diol as a part of a diol component); and others. The diol(s) may be used singly or in combination. Among these diols, the polyester diol, or the polyether diol such as a polytetramethylene ether glycol is used in many cases.

[0064]

As the chain-extension agent, there may be used a glycol [for example, a short chain glycol, e.g., a C_{2-10}alkylene diol such as ethylene glycol, propylene glycol, 1,4-butanediol, or 1,6-hexanediol; bishydroxyethoxybenzene (BHEB)], and in addition a diamine [for example, an aliphatic diamine such as a C_{2-10}alkylenediamine, e.g., ethylenediamine, trimethylenediamine, tetramethylenediamine, or hexamethylenediamine; an alicyclic diamine such as isophorone diamine; an aromatic diamine such as phenylenediamine, or xylylenediamine]. The chain-extension agent(s) may be used singly or in combination.

[0065]

The thermoplastic polyurethane-series resin may also include a perfect thermoplastic polyurethane obtained by using a diol and a diisocyanate at a substantially equivalent amount, in addition an imperfect or terminal isocyanate-group containing thermoplastic polyurethane having a small amount of a residual free (or unreacted) isocyanate, which is obtained by using a slightly excess amount of a diisocyanate relative to a diol, and a terminal

hydroxyl-group containing thermoplastic polyurethane obtained by using a slightly excess amount of a diol relative to a diisocyanate.

[0066]

Among the thermoplastic polyurethane-series resins, in particular, it is preferred the thermoplastic polyurethane elastomer which is obtained by using a diol (e.g., a diol having a polyester unit or a polyether unit), a diisocyanate, and a glycol (e.g., a short chain glycol) as the chain-extension agent. The thermoplastic polyurethane elastomer comprises a hard segment (hard block) which is composed of a polyurethane with the use of a glycol and a diisocyanate, and a soft segment (soft block) composed of an aliphatic polyether diol (e.g., a poly(oxyethylene) glycol), an aliphatic polyester diol or others. The polyurethane elastomer may include a polyester urethane elastomer, a polyether urethane elastomer, and others, depending on the species of the soft segment.

[0067]

These thermoplastic polyurethane-series resins can be used singly or in combination.

[0068]

In such a range that the effects of the present invention are not deteriorated, the thermoplastic polyurethane-series resin member may comprise other resin(s) (e.g., a thermoplastic resin, particularly a thermoplastic elastomer such as a polyamide-series

elastomer, a polyester-series elastomer, or a polyolefinic elastomer), a stabilizer (e.g., a heat stabilizer, an ultraviolet ray absorbing agent, an antioxidant), a plasticizer, a lubricant, a filler, a coloring agent, a flame retardant, an antistatic agent, and others.

[0069]

In the molded composite article, since the polyamide-series resin has an alicyclic ring, the polyamide-series resin firmly joins or bonds with the thermoplastic polyurethane-series resin without using an adhesive. The bonded strength or joined strength is usually not less than 30 N/cm, and cohesive failure sometimes occurs along with separation of the polyamide-series resin member (e.g., a hard resin member) from the thermoplastic polyurethane-series resin member (e.g., a soft resin member). The bonded strength of such a molded composite article is usually 30 N/cm to cohesive failure, preferably not less than 40 N/cm, and particularly not less than 50 N/cm (not less than 50 N/cm to cohesive failure).

[0070]

[Production process of molded composite article]

The molded composite article of the present invention may be produced by joining the polyamide-series resin with the thermoplastic polyurethane-series resin under heating. The joining may be usually ensured by heating at least one resin selected from the polyamide-series resin and the thermoplastic polyurethane-series resin to be molten, and

bringing one resin in the molten state into contact with the other resin. Such a molded composite article may be produced by joining the polyamide-series resin with the thermoplastic polyurethane-series resin in a molding process by means of a conventional molding method such as a thermoforming (e.g., a heat press molding, an injection press molding), an injection molding (e.g., an insert injection molding, a two-color (or double) injection molding, a core-back injection molding, a sandwich injection molding), an extrusion molding (e.g., a co-extrusion molding, a T-die lamination molding), or a blow molding.

[0071]

For example, in a molding method such as an insert molding or an injection press molding, the both resins may be joined together by heating and melting the thermoplastic polyurethane-series resin, and molding the thermoplastic polyurethane-series resin in a molten state with contacting with at least a part of a resin member composed of the polyamide-series resin. The both resins may also be joined together by heating the polyamide-series resin to be molten, and bringing the polyamide-series resin in the molten state into contact with at least a part of a resin member composed of the thermoplastic polyurethane-series resin. Moreover, in a molding method such as a double injection molding or a co-extrusion molding, joining of the both resins may be ensured by heating and melting both the polyamide-series resin and the thermoplastic polyurethane-series resin

differently, and molding the molten polyamide-series resin and the molten thermoplastic polyurethane-series resin with contacting with each other. A molded composite article in which the polyamide-series resin member is firmly joined to the polyurethane-series resin member can be obtained by melting at least one resin selected from the polyamide-series resin and the polyurethane-series resin, bringing the polyamide-series resin into contact with the thermoplastic polyurethane-series resin for joining, and usually cooling the resulting matter. Moreover, depending on a purpose and an application, it is sufficient to join the polyamide-series resin member to the thermoplastic polyurethane-series resin member at least in part.

[0072]

Incidentally, the resin can be molten by heating to a temperature of not less than a melting point thereof. In the case of a substantially uncrystallized resin, the resin can be molten by heating to a temperature of not less than a glass transition point (Tg) thereof.

[0073]

According to the present invention, since the polyamide-series resin contains an alicyclic ring and the alicyclic ring acts on the thermoplastic polyurethane-series resin, the bonded strength can be significantly improved even in a molded composite article obtained from a different kind of materials, and such a high-level bonded strength cannot be obtained from a

physical action caused by simple thermal fusing or welding. Thus, the present invention can also provide high freedom of choice of the species of the polyurethane-series resin, for example both polyether-series polyurethane and polyester-series polyurethane can be used without any distinction.

[0074]

As described above, it is not particularly limited which of the resins between the polyamide-series resin and the polyurethane-series resin is molten. A soft resin (the polyurethane-series resin) having a usually lower melting point or glass transition point (Tg) may be heated, and may be joined to a hard resin member comprising a hard resin (the polyamide-series resin) having a higher melting point or Tg. Moreover, a hard resin (the polyamide-series resin) having a generally higher melting point or Tg may be heated, and may be joined to a soft resin member comprising a soft resin (the polyurethane-series resin) having a lower melting point or Tg.

[0075]

Among these methods, in particular, the former method has an advantage over conventional techniques since the effects of the present invention are characteristically and effectively exhibited. In the conventional method using simple physical thermal fusing, when letting a precedently molded polyamide-series resin member joined with a followingly molding polyurethane-series resin, the

molding temperature of the polyurethane-series resin becomes lower than the melting point of the precedently molded polyamide-series resin in many cases, and therefore thermal fusing is difficult to proceed. Moreover, even when the molding temperature of the polyurethane-series resin is higher than the melting point of the polyamide-series resin, the heat quantity is often insufficient to melt the surface of the polyamide-series resin member. Therefore, the conventional techniques usually never comprise such a manner as molding the polyamide-series resin member before molding the polyurethane-series resin. However, according to the present invention, even in such a case, the polyamide-series resin member and the thermoplastic polyurethane-series resin can be more easily joined together by an action of the amino group contained in the polyamide-series resin. Accordingly, the present invention can increase the freedom of the production process of the composite article and can also rationalize the process step to a large degree. Moreover, even in the species of the polyurethane resin is freely chosen with no distinction between polyether-series and polyester-series polyurethane resins, thereby such a resin composition extremely contributes to reductions in material cost.

[0076]

According to the present invention, although the hard resin usually comprises the polyamide-series resin having an alicyclic ring and the soft resin usually comprises the

thermoplastic polyurethane-series resin in practical cases, the hard resin may comprise the thermoplastic polyurethane-series resin and the soft resin may comprise the polyamide-series resin. Moreover, the hardness of the polyamide-series resin may be the same level as that of the thermoplastic polyurethane-series resin.

[0077]

To be more precise, in the heat press molding, a molded composite article may be produced by melting at least one resin of the hard resin (or composition) and the soft resin (or composition) in a metal mold of the press molding, bringing the both resins into contact with each other under an applied pressure, and joining the resins to each other. In the heat press molding, the hard resin and/or the soft resin may be filled in the metal mold in a pellet form, a powdered form or other form(s), or may be loaded to the metal mold as a molded article precedently formed by other molding method.

[0078]

In the insert injection molding, a molded composite article may be produced by molding any one of the hard resin (or resin composition) or the soft resin (or resin composition) with the use of a molding method (such as an injection molding, an extrusion molding, a sheet molding, or a film molding), inserting or putting thus shaped molded article in a metal mold, and then injecting the other resin to the space or cavity between the molded article and the

metal mold. In the insert injection molding, the molded article to be inserted in the metal mold is preferably pre-heated.

[0079]

In the two-color (or double) injection molding, a molded composite article may be produced by injecting any one component of the hard resin (or resin composition) or the soft resin (or resin composition) to a metal mold by means of two injection molding machines or more, and exchanging cavity of the metal mold by rotation or movement of the metal mold, and injecting the other component to the space or cavity between thus obtained molded article and the metal mold.

[0080]

In the core-back injection molding, a molded composite article may be produced by injecting any one component of the hard resin (or resin composition) or the soft resin (or resin composition) in a metal mold, enlarging the cavity of the metal mold, and injecting the other component to the space or cavity between thus obtained molded article and the metal mold.

[0081]

Among these molding methods, particularly from the viewpoint of mass production or other properties, suitable methods are, for example, the heat press molding such as injection press molding, and the injection molding (e.g., insert injection molding, double injection molding,

core-back injection molding, sandwich injection molding).

[0082]

In the thermal fusing, the melting temperature (or thermal fusing temperature) of the hard resin and/or soft resin may be selected depending on the species of the both resins (or resin compositions), and may for example be about 100 to 250°C, preferably about 120 to 230°C, and more preferably about 150 to 220°C.

[0083]

The structure and configuration of the molded composite article is not particularly limited to a specific one, and may be a structure suitable for design, decorative property, touch or others. For example, such a structure may be obtained by coating or laminating a part or all of the soft resin member with the hard resin member, and usually, preferably obtained by coating or laminating a part or all of the hard resin member with the soft resin member (for example, obtained by coating part of the hard resin member, which contacts with human body (such as a hand), with the soft resin member). Moreover, the concrete structure includes, for example, a two-dimensional structure (such as a sheet-like form, or a plate-like form), and a three-dimensional structure (such as a stick-like form, a tube-like form, a casing, or a housing).

[0084]

According to the present invention, the hard resin and the soft resin can be directly and firmly joined together

by thermal fusing without (going through) complicated production steps (e.g., a step for creating a concavo-convex site in the composite area, a step for coating an adhesive). Therefore, the present invention ensures to obtain a lightweight and strong molded composite article improved in properties such as design, decorative property, or good touch or texture (e.g., soft texture, flexibility).

[Industrial Applicability]

[0085]

The molded composite article of the present invention may be used as various industrial components (or parts), for example, an automotive part (e.g., an automotive interior part such as an instrument panel, a center panel, a center console box, a door trim, a pillar, an assist grip, a steering wheel, or an air bag cover; an automotive exterior part such as a lacing, or a bumper; and an automotive functional component such as a rack and pinion boot, a suspension boot, or a constant velocity joint boot), a household electrical part (e.g., a cleaner bumper, a switch of a remote control, and a key top of office automation (OA) apparatus), a product to be used in water (e.g., swimming goggles, and a cover of a underwater camera), an industrial part (a cover part; various industrial parts equipped with a packing for the purpose of sealing property, water proofing property, sound insulating property, vibration insulating property, or other properties; and an industrial rubber roller), an electric or electronic device part (e.g., a

curl cord wire covering, a belt, a hose, a tube, and a sound deadening gear), sports goods, shoes goods (e.g., athletic shoes, a shoe sole), and a part requiring design or decorative property (e.g., dark glasses and glasses).

[0086]

Among them, the molded composite article is particularly suitable for a constitutive member of the shoe or the mechanical part such as the roll (e.g., a rubber roller). The constitutive member of the shoe includes a shoe sole (sole), and others. Moreover, the molded composite article may form (or constitute) athletic shoes, work shoes (e.g., boots, rain shoes, shoes for gardening). In such a shoe application, a combination of a hard or glass fiber-reinforced polyamide-series resin and a soft polyurethane-series resin, which was difficult in the past, becomes easy, and the molded composite article greatly contributes to improvement in design or functionality of the shoe.

[0087]

Further, in the roll (e.g., a rubber roller) application, for example, the roll may comprise an axis (shaft) in which at least the surface layer comprises a polyamide-series resin, and a thermoplastic polyurethane-series resin layer formed along the surrounding surface of the axis. The axis may be obtained by forming a polyamide-series resin layer on the surface of the metal shaft, or may be an axis comprising a

polyamide-series resin. In such a roller application, since a cutting finish for obtaining a shaft precision and a surface finish of a thermoplastic polyurethane-series resin can be conducted in one operation by the same grinding machine, the production process of the roller can be significantly abbreviated and the cost can be exponentially reduced.

[Examples]

[0088]

The following examples are intended to describe this invention in further detail and should by no means be interpreted as defining the scope of the invention.

[0089]

(Evaluation of thermal fusing)

The molded composite articles obtained in Examples were cut into a size of 20 mm in width and 100 mm in length. In each cut piece, the tensile test was conducted by drawing a tong hold to 180° direction at a drawn speed of 20 mm/minute. Through the tensile test, the peel strength in the fusing interfaces between a polyamide member and a polyurethane elastomer member was measured. On the basis of the peel strength, the thermal fusing property (bonded strength) between the polyamide member and the polyurethane elastomer member was evaluated.

[0090]

In general, with respect to adhesive strength, the peel in which a peel strength is less than 50 N/cm is usually

regarded as an interfacial peel. In such a case, the adhesion is determined as binding defective in many purposes because the bonded matter can be peeled by hand. The peel in which a peel strength is over 50 N/cm falls under the realm of peel including a cohesive failure. Namely, the bonded matters is scarcely peelable to be peeled by hand, and such a bonded strength is sufficiently adaptable for industrial purposes. The peel in which a peel strength from 80 N/cm and to 100 N/cm falls under a cohesive failure throughout the molded article, and the molded article is suitable for purposes including an athletic shoe to endure severe bending fatigue.

[0091]

Example 1

In an autoclave substituted with nitrogen gas, a salt (1000g) of bis(4-aminocyclohexyl)methane and dodecanedicarboxylic acid was heated at 220°C under an applied pressure (1.7 MPa), and water in the reaction system was discharged with the nitrogen gas from the reaction system over 4 hours. Subsequently, the temperature of the system was gradually increased up to 275°C, and residual water was perfectly removed to outside of the system. Thereafter, the inner pressure of the autoclave was reduced to an atmospheric pressure. After cooling, a transparent polyamide (polymer 1) having a number average molecular weight of about 23000 and a terminal amino group concentration of 43 mmol/kg was obtained. The ratio of a

monomer residue having an alicyclic amino group relative to other monomer residues in the polymer 1 (hereinafter refers to as "MR value") was calculated as the former/the latter = 50/50.

[0092]

With the polymer 1, a flat plate having 100 mm width, 100 mm long and 2 mm thick was produced by an injection molding, and the surface of one-fifth in the above polyamide molded article (about 20 mm width from the edge) was covered with an aluminum foil. Subsequently, the covered article was placed in a flat metal mold having 100 mm width, 100 mm long and 4 mm depth, and the thermoplastic polyurethane resin was injected into the void of the metal mold. The injection molding of the polyurethane resin was conducted at a cylinder temperature of 205°C and a metal mold temperature of 60°C. Incidentally, two kinds of the polyurethane resins were used, that is, polyether-series polyurethane resin (produced by BASF, Erastollan, 1195ATR) and polyester-series polyurethane resin (produced by BASF, Erastollan, ET195). The molded composite articles obtained from each of the polyurethane resins were cut into a size of 20 mm in width, and the peeling test was conducted using the part covered with an aluminum foil as a tong hold. The results are shown in Table 1.

[0093]

Comparative Example 1

A polymerization was conducted in the same manner

as in Example 1 except that hexamethylenediamine was used instead of bis(4-aminocyclohexyl)methane. The obtained polyamide 612 (polymer 2) had a number average molecular weight of about 20000, and a terminal amino group concentration of 51 mmol. The MR value of the polyamide 612 (polymer 2) was 0/100. The peeling test between the polymer 2 and the polyurethane resin was conducted in the same manner as in Example 1. The results are shown in Table 1.

[0094]

Example 2

In an autoclave in which the air had been substituted with nitrogen gas, ω-lauryllactam (1000 g), dodecanedicarboxylic acid (15 g), and a small amount of phosphoric acid were heated at 250°C under an applied pressure (1.8 MPa) with stirring. After 4 hour stirring, into the resultant mixture was added bis(4-aminocyclohexyl)methane, and the reaction was further continued at 280°C for 0.5 hour. Then the reaction mixture was started to be cooled, and a polyamide 12 (polymer 3) having cyclohexylamino group in a terminal thereof was obtained. The polyamide 12 (polymer 3) had a number average molecular weight of about 15000 and a terminal amino group concentration of 60 mmol/kg. The MR value was calculated as 1.2/98.8. The peeling test between the polymer 3 and the polyurethane resin was conducted in the same manner as in Example 1. The results are shown in Table 1.

[0095]

Comparative Example 2

In an autoclave in which the air had been substituted with nitrogen gas, ω-lauryllactam (1000 g), dodecanedicarboxylic acid (15 g), and a small amount of phosphoric acid were heated at 250°C under an applied pressure (1.8 MPa), and water in the system was discharged outside of the system with nitrogen gas over 4 hours with stirring. Subsequently, the temperature of the system was leisurely increased up to 275°C, and water remaining in the system was completely removed out of the system. Then the inside pressure of the autoclave was returned to a normal pressure. After cooling, a polyamide 12 (polymer 4) having a number average molecular weight of about 15000 was obtained. The polyamide 12 (polymer 4) had a terminal amino group of an aliphatic chain amino group, and the terminal amino group concentration was 7 mmol/kg.

The MR value of the polymer 4 was 0/100. The peeling test between the polymer 4 and the polyurethane resin was conducted in the same manner as in Example 1. The results are shown in Table 1.

[0096]

Example 3

The transparent polyamide (polymer 1) (60 parts by weight) obtained in Example 1 was mixed with the polyamide 12 (polymer 4) obtained in Comparative Example 2 (40 parts by weight), and the mixture was kneaded with a biaxial

extruder to obtain a polyamide alloy (polymer 5). The polyamide alloy (polymer 5) had a terminal amino group concentration of 29 mmol, and the MR value of 29/71. The peeling test between the polymer 5 and the polyurethane resin was conducted in the same manner as in Example 1. The results are shown in Table 1.

[0097]

Example 4

The alicyclic amino group-containing polyamide 12 (polymer 3) (40 parts by weight) obtained in Example 2 was mixed with the polyamide 12 (polymer 4) obtained in Comparative Example 2 (40 parts by weight) which did not have the alicyclic amino group, and the mixture was kneaded with a biaxial extruder to obtain a polyamide 12 mixture (polymer 6). The polyamide 12 mixture (polymer 6) had a terminal amino group concentration of 28 mmol, and the MR value of 0.4/99.6. The peeling test between the polymer 4 and the polyurethane resin was conducted in the same manner as in Example 1. The results are shown in Table 1.

[0098]

Example 5

A polyamide elastomer (manufactured by Degussa, Vestamid E47S3) (80 parts by weight) was mixed with the polyamide 12 (polymer 3) (20 parts by weight) obtained in Example 2, and the mixture was kneaded with a biaxial extruder to obtain a blended polyamide elastomer (polymer 7). The mixed polyamide elastomer (polymer 7) had a terminal amino

group concentration of 15 mmol, and the MR value of 0.14/99.86. The peeling test between the polymer 8 and the polyurethane resin was conducted in the same manner as in Example 1 except that a polyether-series polyurethane resin (manufactured by BASF, Erastollan, ET880) and a polyester-series polyurethane resin (manufactured by Japan Polyurethane Industry Co. Ltd., Mirastollan E585) were used as a polyether-series polyurethane resin and a polyester-series polyurethane resin, respectively. The results are shown in Table 1.

[0099]

Comparative Example 3

The peeling test between a polyamide elastomer (manufactured by Degussa, Vestamid E47S3) and a polyurethane resin was conducted in the same way with Example 5, and the obtained results are shown in Table 1. The terminal amino group concentration of the used polyamide elastomer was 4 mmol/kg, and the MR value was 0/100.

[0100]

[Table 1]

Table 1

	Polymer	Terminal amino group concentration	MR value	Peel strength N/cm	
				Polyether-series polyurethane	Polyester-series polyurethane
Example 1	Polymer 1	43	50/50	140	133
Comparative Example 1	Polymer 2	51	0/100	70	62
Example 2	Polymer 3	60	1.2/98.8	130	145
Comparative Example 2	Polymer 4	7	0/100	15	10
Example 3	Polymer 5	29	29/71	112	127
Example 4	Polymer 6	28	0.4/99.6	70	58
Example 5	Polymer 7	15	0.14/99.86	95	76
Comparative Example 3	E47S3	4	0/100	90	24

[0101]

As shown in the results in Table 1, the molded composite articles of Examples showed high peel strength independent of kinds of polyurethane. On the contrary, molded composite articles of Comparative Examples 1 and 2 showed low peel strength, and the sheet of Comparative Example 3 had low peel strength to the polyester-series polyurethane.

[Document Name] Abstract

[Abstract]

[Object(s)] To achieve a direct and firm bonding between a polyamide-series resin member and a thermoplastic polyurethane-series resin member which were different in properties from each other by a simple process.

[Means to Solve the Problems] In a molded composite article, a resin member comprising a polyamide-series resin and a resin member comprising a thermoplastic polyurethane-series resin are directly joined with each other; and a polyamide-series resin comprising a polyamide component having an alicyclic ring is used as the polyamide-series resin. The polyamide component may be an alicyclic polyamide-series resin or an alicyclic polyamide elastomer, or a combination of an alicyclic polyamide component (such as an alicyclic polyamide-series resin, an alicyclic polyamide elastomer, or an alicyclic polyamide oligomer) (particularly, a polyamide component obtained by using an alicyclic diamine) and a non-alicyclic polyamide component. The molded composite article can be produced by heating at least one of the polyamide-series resin and the thermoplastic polyurethane-series resin to join these resins with each other.

[Selected Fig.] none

Applicant Record

Identification No.	[000108982]
1. Date of Alternation	July 12, 2001
[Reason of Alternation]	change of name
Address	2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo
Name	Daicel-Degussa, Ltd.
2. Date of Alternation	May 11, 2004
[Reason of Alternation]	change of address
Address	18-1, Konan 2-chome, Minato-ku, Tokyo
Name	Daicel-Degussa, Ltd.